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Dinitrogen as a probe of acid sites of zeolites

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Nitrogen adsorption on H-ZSM-5 and H-Y zeolites at low temperatures were studied by in situ FT-IR spectroscopy. For each zeolite, two absorption bands were observed at around 2334 and 2352 cm^{-1} in the ν(NN) region and were assigned to the ν(NN) mode of dinitrogen species adsorbed on Brønsted and Lewis acid sites of the zeolites, respectively. These results and previous results for H-mordenite suggest that dinitrogen serves as a probe of acid sites and its advantages as probe are discussed.

Keywords: N_2 adsorption; FT-IR; H-ZSM-5; H-Y; acid sites

1. Introduction

The acid sites of zeolites play an important role in the catalytic process over zeolites and their properties have been studied using various techniques [1]. Pyridine and ammonia act as useful probes of acid sites and are routinely used nowadays in infrared (IR) [2] and temperature programmed desorption (TPD) [3] studies. They are, however, strong bases compared with the reactants which participate in practical catalytic reactions and interact even with weak acid sites which are not responsible for the reactions [4,5]. It is favorable to use weaker bases to identify the actually active acid sites. Further, the molecular diameter of pyridine is rather large to probe the acid sites embedded in the narrow channel of zeolites and smaller-sized probes are required [6]. Although small and weakly basic molecules such as H_2 [7] and CO [8–10] have recently been used as IR-spectroscopic probes of the acid sites, the proposition of another probe molecule is highly beneficial for the investigation of the acid sites of solids.

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We have recently reported the IR-spectroscopic observation of two kinds of dinitrogen species adsorbed on Brønsted and Lewis acid sites of H-mordenite [11]. Nitrogen molecule has a lower proton affinity (494.5 kJ/mol) compared with pyridine (924 kJ/mol) and ammonia (853.5 kJ/mol) and is regarded as a very weak base [12]. Further, its molecular diameter is smaller than that of pyridine which makes it an excellent candidate as the probe of acid sites. Actually, N_2 was recently used as probe of Lewis acid sites of H-ZSM-5 in a ^{15}N-NMR study [13]. We are investigating the nitrogen adsorption on H-ZSM-5 and H-Y zeolites to confirm that dinitrogen can be used as the probe of acid sites of zeolite. In this letter, we report the effect of the sample-pretreatment condition on the infrared absorption bands of adsorbed N_2 species and discuss the advantages of dinitrogen as a probe.

2. Experimental

H-ZSM-5 (Si/Al = 48) provided by Professors Tatsuaki Yashima of Tokyo Institute of Technology and Seitaro Namba of the Nishi Tokyo University and H-Y zeolite JRC-Z-HY5.6 (Si/Al = 2.8) by the Catalysis Society of Japan were used. The self-supporting disks (typical density was between 8 and 10 mg/cm^2) of the zeolites were placed in a quartz cell which in turn was attached to a closed circulation system. The design of the cell, which allows us in situ sample treatment and IR-measurement in the temperature range between 95 and 1000 K, is similar to that described elsewhere [14]. The conditions of sample pretreatment are described in section 3. Gas pressure under 1.3 kPa was measured by a high-precision capacitance gauge (Baratron type 122A) and the residual pressure obtained after evacuating the sample is less than 0.1 Pa (estimated to be less than 10^{-3} Pa). Nitrogen gas (99.9%) was purified by passing slowly through a cold trap at liquid nitrogen temperature to remove residual water and other impurities. D_2O with the purity of 99.9 at% in D content was purchased from Isotec Inc., USA and used after degassing in vacuum. Infrared measurements were performed using a Jasco FT/IR-7000 spectrometer equipped with an MCT detector at the resolution of 2 cm^{-1} and at the averaging of 128 scans under the condition of equilibrium pressure. FT-IR spectra of the clean disk were measured at low temperatures and used as background spectra. IR spectra in the ν(NN) and ν(OH) region were derived in the form of difference and as-observed spectra, respectively.

3. Results and discussion

3.1. N_2 ADSORPTION ON H-ZSM-5

Fig. 1 shows the effect of the sample-pretreatment temperature on the IR spectrum of the ν(NN) region. The sample disk was evacuated at 773 K for 1 h and then

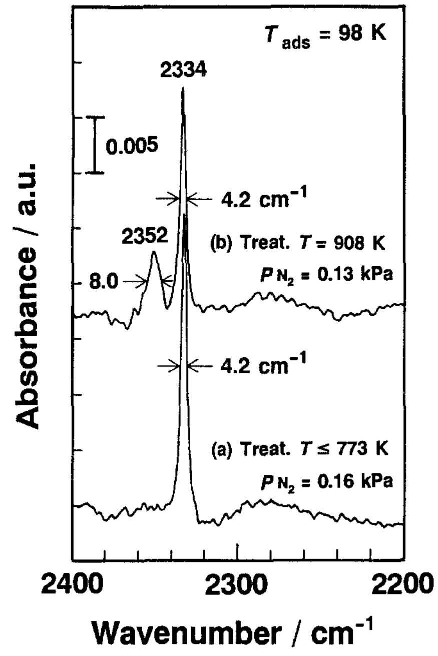

Fig. 1. Effect of pretreatment temperature on the ν(NN) bands observed for the N_2 adsorption on H-ZSM-5 at 98 K. (a) The sample disk was evacuated at 773 K for 1 h and treated with O_2 of 12 kPa for 1 h followed by the evacuation for 1 h at the same temperature. P_{N_2} = 0.16 kPa. (b) After (a), the sample was evacuated at 908 K for 15 min. P_{N_2} = 0.13 kPa.

treated with O_2 of 12 kPa for 1 h followed by evacuation for 30 min at the same temperature. The thus treated disk was exposed to N_2 gas of 0.16 kPa at 98 K and its IR spectrum gave a single absorption band at 2334 cm^{-1} as shown in fig. 1a. When the thus treated disk was evacuated at 908 K for 15 min and was exposed to N_2 of 0.13 kPa at 98 K, an additional absorption band was observed at 2352 cm^{-1} as shown in fig. 1b. Fig. 2 shows the spectral change of the ν(OH) region observed for the same sample disk under different pressures of N_2. The dashed line shows the ν(OH) band of clean H-ZSM-5 pretreated by the evacuation at 908 K, and the dashed–dotted line and the solid line show that of H-ZSM-5 exposed to N_2 of 0.04 and 0.13 kPa, respectively. On increasing the N_2 pressure, the ν(OH) band at 3619 cm^{-1} which is due to the acidic OH groups of H-ZSM-5 [15] decreased and a new ν(OH) band grew at 3499 cm^{-1}. The 3619 cm^{-1} band diminished almost completely at the N_2 pressure of 0.13 kPa, where the increase in intensity of the ν(NN) band at 2334 cm^{-1} saturated. On the other hand, the ν(OH) band at 3753 cm^{-1}, which is due to isolated and terminal silanol groups located outside the crystals and, possibly, internal defects [10], was almost unaffected by the adsorption of N_2 consistent with the very weak acidity of the silanol groups.

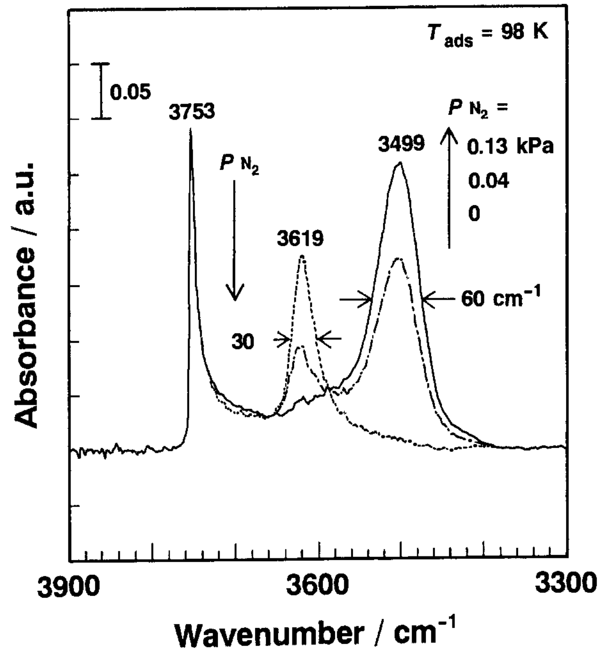

Fig. 2. Spectral change of ν(OH) bands of H-ZSM-5 under different pressure of N_2 at 98 K after evacuation at 908 K for 15 min. (- - -) P_{N_2} = 0 kPa, (– · –) P_{N_2} = 0.04 kPa, (——) P_{N_2} = 0.13 kPa.

The above observations are in agreement with our previous results on the N_2 adsorption on H-mordenite [11] in the following respects. First, two ν(NN) bands were observed at 2335 and 2352 cm^{-1} which were attributed to the N_2 species adsorbed on the Brønsted and Lewis acid sites, respectively (we hereafter denote these species by *species B* and *species L*, respectively). Secondly, the 2335 cm^{-1} band was accompanied by the decrease of the ν(OH) band at 3616 cm^{-1} which was attributed to the acidic OH groups and by the growth of new ν(OH) band at 3510 cm^{-1}. This feature was explained by the formation of hydrogen bonds between N_2 and the acidic OH groups. Thirdly, the 2352 cm^{-1} band was observed for the sample evacuated at above 773 K (especially above 873 K) but was not observed for the sample pretreated with D_2O vapor with subsequent evacuation at 573 K. The ν(NN) bands at 2334 and 2352 cm^{-1} observed here were accordingly attributed to species B and species L, respectively.

3.2. N_2 ADSORPTION ON H-Y ZEOLITE

Fig. 3 shows the spectra observed for H-Y zeolites. Each N_2 adsorption was performed under a pressure of 6.7 kPa at 150 K. The sample disk was evacuated at 773 K for 30 min and was exposed to N_2. Its IR spectrum in the ν(NN) region was

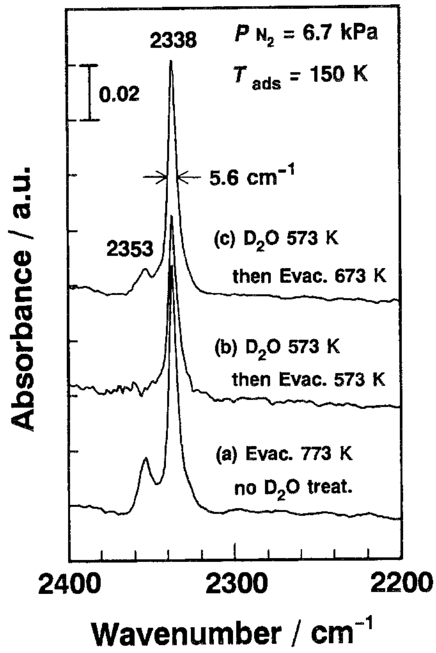

Fig. 3. Effects of D_2O-vapor pretreatment and evacuation temperature on ν(NN) bands observed for the N_2 adsorption on H-Y zeolite at 150 K. $P_{N_2} = 6.7$ kPa. (a) After evacuation at 773 K for 30 min, (b) the sample in (a) was treated with D_2O vapor of 1.2 kPa for 30 min followed by the evacuation for 30 min at 573 K, and (c) the sample in (b) was evacuated at 673 K for 1 h.

shown in fig. 3a. Two absorption bands were observed at 2353 and 2338 cm^{-1} and are assigned to the ν(NN) band of species L and species B, respectively, in accordance with the assignment of the bands observed for H-mordenite [11] and H-ZSM-5. The assignment was confirmed by the following observations: after the measurement of the spectrum shown in fig. 3a the sample disk was treated with D_2O vapor of 1.2 kPa for 30 min and then was evacuated for 30 min at 573 K, and the thus treated disk was exposed to N_2 and gave the spectrum shown in fig. 3b. The D_2O-vapor pretreatment is known to reduce the Lewis acid sites [16], and the 2353 cm^{-1} band disappeared as seen in fig. 3b. This sample disk was next evacuated at 673 K for 1 h to revive the Lewis acid sites by dehydration at higher temperature [16]. The exposure to N_2 gave the spectrum shown in fig. 3c, and it is seen that the 2353 cm^{-1} band recovered its intensity indicating the partial reproduction of Lewis acid sites by the evacuation. The fact that H-Y zeolite and H-mordenite gave the 2352 cm^{-1} band of species L although H-ZSM-5 did not when evacuated at 773 K indicates that higher evacuation temperature is necessary for the production of enough amount of Lewis acid sites on H-ZSM-5 than that needed on H-Y and H-mordenite.

3.3. USABILITY AND ADVANTAGES OF N_2 AS A PROBE OF ACID SITES

We have revealed that N_2 molecule gives characteristic IR bands when it interacts at low temperatures specifically with Brønsted acid sites of Lewis acid sites of the zeolites regardless of their structure, and this fact implies that the ν(NN) bands of the adsorbed N_2 species serve as the versatile probe of the acid sites. Knözinger discussed the use of *specific poisoning* of active sites of oxide surfaces for the characterization of active sites and the improvement of the catalytic selectivity toward a desired product, and enumerated the criteria for the selection of suitable poisons [4]. Seen as the probe of acid sites, N_2 has several advantages compared with the conventionally used pyridine and ammonia. On referring to the criteria given by Knözinger, N_2 probe has the following characteristics:

(1) *Specific interaction.* N_2 preferentially interacts with both Brønsted and Lewis acid sites of zeolite to give the ν(NN) bands at around 2335 and 2352 cm^{-1}, respectively. The separation of the two bands is well outside of the spectral resolution of a conventional spectrometer.

(2) *Detectability of surface species.* There is no interference from the gas phase absorption band because it is forbidden to free molecules while another candidate, CO, has the quite strong absorption band of gaseous CO which has to be subtracted to isolate the spectrum of adsorbed species.

(3) *Molecular size.* N_2 is smaller than pyridine in molecular diameter so that N_2 has better access to narrower space. There are many cases for zeolites [6] where the detected density of Lewis acid sites is affected by steric hindrance [17]. N_2 will serve in discriminating the steric or size effect.

(4) *Strength of interaction.* Reactants which participate in the practically executed catalytic reaction over zeolites are very weak bases in most cases so that only the strongest acid sites are responsible for the catalytic function. Ammonia and pyridine, strong bases in gas phase, are known to interact with weak acid sites, which is not responsible for the catalysis too [4,5]. N_2 on the other hand can be considered as a very weak base so that it interacts with and thus probes only the strong acid sites. In this respect, the comparison between CO and N_2 is very interesting. CO has a slightly higher proton affinity (594 kJ/mol) than N_2 (494.5 kJ/mol) [12] and has been recently used as a versatile probe of Brønsted and Lewis acid sites [8–10]. Recently, Zecchina et al. studied extensively the interaction of CO with Na- [9] and H-ZSM-5 [10] at 77 K and found that CO interacts even with the silanol groups as well as with the acidic bridged-hydroxyl groups. The silanol groups have very weak acidity and hardly interact with N_2 as revealed by this work. This fact shows clearly that N_2 probes only the strong acid sites and gives a new measure of acid strength of acid sites.

(5) *Removability.* The rather weak interaction of N_2 with zeolites enables us to remove the adsorbed N_2 by simply evacuating at low temperature. This also means that the contamination of sample and apparatus can be made minimal.

(6) *Reactivity and surface reconstruction.* N_2 is chemically very inert compared

with pyridine or ammonia and the catalytic function of zeolites is least affected in the course of their characterization.

The detailed features of N_2 adsorption on H-ZSM-5 and H-Y will be published elsewhere [18].

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